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LONG CHAIN PHENOLS FROM THE BURMESE LAC TREE, *MELANORRHOEA USITATE*

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Key Word Index—*Melanorrhoea usitate*; Anacardiaceae; lac tree; sap; composition; long-chain phenols.

Abstract—Twenty eight constituents of the sap of the Burmese lac tree, *Melanorrhoea usitate* have been identified. The sap consists of homologues of thitsiol (*ca* 20%), laccol (*ca* 10%), urushiol (4%), 3-substituted catechols with 12-phenyldodecyl (*ca* 30%) or 10-phenyldecyl groups (*ca* 8%), 4-substituted catechols (*ca* 3%) and 5-substituted resorcinols (*ca* 1%) with the same substituents. 3-Substituted phenols with characteristic side chain groups are also contained in smaller amount. The biosynthetic route of these secondary plant metabolites, especially of novel phenolic lipids with ω-phenylalkyl side chains, is discussed.

INTRODUCTION

In most Asian countries, the fluid sap exuded from several kinds of lac trees is used as a preservative surface coating material for valuable wooden, porcelain and metallic wares [1], providing a number of cultural treasures. Sap of the Burmese lac tree, *Melanorrhoea usitate*, is one of the naturally occurring phenolic coating materials. Although intensive studies of Japanese or Chinese lac trees, *Rhus vernicifera* were executed with respect to the composition of urushiol congeners [2–5], the nature of laccase [6] and stellacyanine [7], the structure of plant gum included in the sap [8], and the mechanism of physiological polymerization of the sap [9], little is known about the sap of the Burmese lac tree.

In 1922, Majima reported that 4-substituted catechols having an n-C_{17} alkyl side chain were the main constituents of sap of *M. usitate*, and he named this compound thitsiol (isourushiol) [10]. In the report, it was also pointed out that other saturated substances were included in the sap besides thitsiol in considerably great amounts, although their nature and chemical structures were not elucidated.

We have recently developed a general method to separate and analyse oily sap components of lac trees based on HPLC. Urushiol of the lac tree, *R. vernicifera*, was separated into more than 10 congeners as dimethyl ethers and the structures of olefinic side chains were exactly determined [4]. More recently, satisfactory separation of intact urushiol has been achieved by reversed-phase LC using a weakly acidic eluant, and the structure of each congener has been confirmed by superconducting ^{1}H NMR spectroscopy [5].

By applying this newly attained general methodology, we executed an intensive compositional investigation of the sap of the Burmese lac tree in order to clarify its exact constitution. From this study it has been revealed that the sap consists not only of thitsiol but also a variety of homologues of urushiol, laccol, catechols substituted with an ω-phenylalkyl group at positions 3 or 4 and resorcinols with the same substituent at position 5, which are the first phenolic lipids having a phenyl group in the side chain, and further 3-substituted phenols with characteristic side chains. The biosynthetic route of these secondary plant metabolites is also discussed.

RESULTS AND DISCUSSION

After gel permeation chromatographic separation, the monomeric components of the sap of *M. usitate* was subjected to LC analysis in (i) the methylated and hydrogenated form, (ii) the methylated form and (iii) the intact form.

By reversed-phase chromatography of the methylated and hydrogenated sample, 10 constituents were isolated (Table 1); compounds **6** and **10** were separated by subsequent liquid–solid chromatography (LSC). They were identified as dimethylethers of 4-pentadecylcatechol (**1**), hydrothitsiol (**2**), hydrourushiol (**3**), hydrolaccol (**4**) and ω-phenylalkylcatechols **5–8** and 5ω-phenylalkylresorcinols **9** and **10**.

Compounds **1** and **2** showed IR bands of out-of-plane bending deformation of a 1,2,4-trisubstituted benzene at 810 and 850 cm^{-1}, and veratroles **3** and **4** showed the corresponding IR band of a 1,2,3-trisubstituted benzene at 750 cm^{-1}. Mass spectral data and ^{1}H NMR spectra were consistent with their structures. Catechols **5** and **6** showed an intense IR band of out-of-plane bending deformation of a monosubstituted benzene at 700 cm^{-1} in addition to those due to a 1,2,4-trisubstituted benzene at 810 and 850 cm^{-1}. In the 90 MHz ^{1}H NMR spectra, an apparent singlet of phenyl protons (δ 7.1) was prominent. In the EI mass spectra, the fragment ions of m/z 91 and 151 were observed; the former was assigned to a tropylium ion

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Table 1. Constituents of the sap of the Burmese lac tree, *Melanorrhoea usitate*

Compound*	Content(%)†		R_t§(min)		
	by wt	by GC‡	Methylated ‖	Methylated ¶	Intact**
4-Substituted catechols					
15	2.0	0.7			21.5
16	2.1	nd			22.3
17 (11)	12.4	20.5		27.2	30.2
18	1.4	nd			48.6
19	tr	nd			17.7
20 (1)	1.0	0.7	23.6		51.2
(2)			33.3		
3-Substituted catechols					
21	0.8	nd			24.2
22	0.9	nd			26.0
23 (12)	12.0	19.7		29.6	32.8
24 (13,14)	tr	nd		37.7	51.2
25	tr	nd			57.8
26	tr	nd			12.9
27	tr	nd			32.8
28 (3)	2.7	3.9	25.9	40.0	57.8
(4)			38.4		
ω-Phenylalkylcatechols					
29 (5)	0.5	1.1	9.9		17.7
30 (6)	1.8	3.6	13.3		32.8
31 (7)	8.6	7.5	10.8	22.9	18.8
32 (8)	45.4	36.0	14.6	27.2	34.1
ω-Phenylalkylresorcinols					
33 (9)	0.4	0.7	10.4		12.0
34 (10)	0.3	2.1	13.3		20.5
3-Substituted phenols					
35	tr	nd			45.5
36	tr	nd			29.4
37	tr	nd			29.4
38	0.6	1.2			28.1
39	0.7	nd			45.5
40	0.5	0.4			14.7
41	tr	nd			29.4
42	tr	nd			29.4

*Numbers in parentheses stand for methylated compounds.

†tr, Trace or less than 0.3%; nd, not determined. The discrepancy in contents determined by the two methods may be due to either error in weighing or the different FID response factors of the various constituents.

‡Based on peak areas determined by flame-ionization detection.

§Retention times on reversed-phase LC.

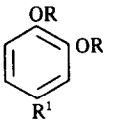
‖Conditions: column, ODS-silica (Unisil Q C-18, 5 μm, 0.8 × 25 cm); eluant, MeCN at 2.0 ml/min; detection, RI.

¶Conditions: column, ODS-silica (Unisil Q C-18, 5 μm, 0.8 × 25 cm); eluant, MeCN–H_2O (8:2 to 9:1) in 20 min at 1.8 ml/min; detection, UV at 254 nm.

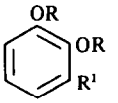
**Conditions: column, ODS-silica (TSK-gel, LS-410, 5 μm, 0.8 × 25 cm); eluant, MeCN–H_2O–HOAc (40:10:1) at 2.5 m;/min; detection, UV at 254 nm.

and the latter to a dimethoxytropylium ion, respectively. From these spectroscopic data, it was concluded that compounds **5** and **6** have a phenyl group in the side-chain end. Similarly, compounds **7**–**10** were revealed to have an ω-phenyl group in the side chains from their IR, ^{1}H NMR and mass spectral data. Their substituted positions in *O*-dimethoxyphenyl nuclei were explicitly determined by IR and ^{1}H NMR spectrometry. Several abundant fractions of the methylated sample were separated by LC (Table 1) and analysed.

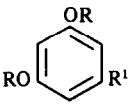
A dienoic compound (**11**) co-eluted with a veratrole homologue (**8**) by reversed-phase HPLC, and was isolated by successive LSC operations. Compound **11** exhibited out-of-plane bending deformation bands at 810 and 850 cm^{-1}. The $[M]^+$ showed it contained two double bonds, both of which are *cis* since no IR peak was detected



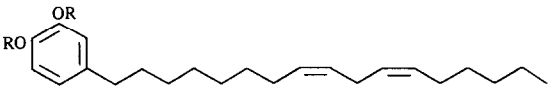
1 R = Me, $R^1 = C_{15}H_{31}$
2 R = Me, $R^1 = C_{17}H_{35}$
5 R = Me, $R^1 = (CH_2)_{10}Ph$
6 R = Me, $R^1 = (CH_2)_{12}Ph$
29 R = H, $R^1 = (CH_2)_{10}Ph$
30 R = H, $R^1 = (CH_2)_{12}Ph$



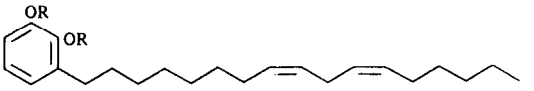
3 R = Me, $R^1 = C_{15}H_{31}$
4 R = Me, $R^1 = C_{17}H_{35}$
7 R = Me, $R^1 = (CH_2)_{10}Ph$
8 R = Me, $R^1 = (CH_2)_{12}Ph$
31 R = H, $R^1 = (CH_2)_{10}Ph$
32 R = H, $R^1 = (CH_2)_{12}Ph$



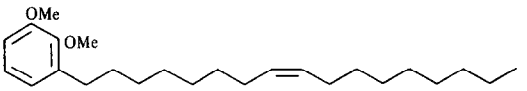
9 R = Me, $R^1 = (CH_2)_{10}Ph$
10 R = Me, $R^1 = (CH_2)_{12}Ph$
33 R = H, $R^1 = (CH_2)_{10}Ph$
34 R = H, $R^1 = (CH_2)_{12}Ph$



11' R = Me
17 R = H



12 R = Me
23 R = H



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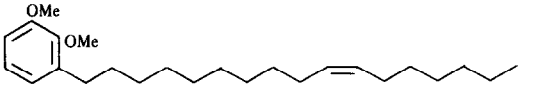

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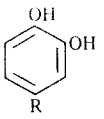
in the region of 900–1000 cm^{-1}. The double bond positions were unambiguously determined to be at C-8′ and C-11′ by reductive ozonolysis followed by LC identification of 2,4-dinitrophenylhydrazones derived from the ozonolysis products of monoolefines obtained by partial hydrogenation of the parent compound [4]. Similarly it was clarified that veratrole **12** has two *cis* double bonds at C-8′ and C-11′. Monoenes **13** and **14** could not be separated, but in the chromatogram of 2,4-dinitrophenylhydrazones derived from the ozonolysis product, those of *n*-nonylaldehyde and *n*-heptylaldehyde were observed along with their corresponding aromatic fragments. As a consequence, the exact side chain structures of the abundant thitsiol (**11**) and laccol (**12**) homologues contained in the sap of the Burmese lac tree were established, and novel lipids **7** and **8** were revealed to have no double bond in their side chains.

The resolution of intact sap was carried out by reversed-phase LC using an acidic eluant (Table 1) permitting the identification of compounds **15–28** (see formulae, where '(*trans*)' signifies that at least one double bond is *trans*).

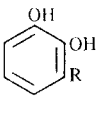
The mass spectra of catechols **15–28** exhibited an intense $[M]^+$ and fragment ions formed by cleavage of the bond β to the aromatic ring (*m/z* 123) and by McLafferty rearrangement (*m/z* 124) of the $[M]^+$ [11].

Compounds **15–20** exhibited out-of-plane bending deformation bands of 1,2,4-trisubstituted benzenes (810 and 850 cm^{-1}), and were identified as congeners of thitsiol. The numbers of carbon atoms and double bonds in the side chain were determined from $[M]^+$ values; homologues **16** and **18** include isolated *trans*-olefin groups as they show an intense IR band at 960 cm^{-1}.

In IR spectra of compounds **21–28**, out-of-plane bending deformation bands characteristic of 1,2,3-trisubsti-



15 R = $C_{17}H_{29}$
16 R = $C_{17}H_{29}$ (*trans*)
18 R = $C_{17}H_{33}$
19 R = $C_{15}H_{29}$
20 R = $C_{15}H_{31}$



21 R = $C_{17}H_{29}$
22 R = $C_{17}H_{29}$ (*trans*)
24 R = $C_{17}H_{33}$
25 R = $C_{17}H_{33}$ (*trans*)
26 R = $C_{15}H_{27}$
27 R = $C_{15}H_{29}$
28 R = $C_{15}H_{31}$

tuted benzenes were observed at 730 and 770 cm^{-1}. From $[M]^+$ values, compounds **21**–**25** were identified as congeners of laccol and **26**–**28** as those of urushiol.

Compounds **19** and **25**–**27** were obtained as mixtures with other compounds but were characterized by GC-MS. They also showed $[M]^+$ ions, a dihydrobenzyl ion (*m/z* 123) and a cyclohexadienyl ion (*m/z* 124). The positions of substitution could not be determined from the data, but were provisionally identified on the basis of their retention times (Table 1).

Compounds **29**–**34** showed very simple mass spectra, where only an $[M]^+$, *m/z* 123, 124 and 91 ions were prominent. The presence of *m/z* 123 and 124 ions indicates that these compounds are derivatives of a dihydric phenol. As the *m/z* 91 ion indicates a tropylium ion derived from a monoalkylbenzene, an alkylphenyl group is also included. This was confirmed by the existence of an intense IR band for a monosubstituted benzene (700 cm^{-1}). The substituted positions of the dihydric phenol nuclei in these compounds were determined from characteristic IR bands of out-of-plane bending deformation of the benzene rings. In the ^1H NMR spectra of homologues **31** and **32** there appeared superimposed triplets due to methylene protons at 1′ and 10′ (or 12′) positions (δ2.59), quintets from methylene protons at 2′ and 9′ (11′) positions (δ1.60), two singlets of hydroxyl protons (δ4.95 and 5.08), an apparent singlet of protons of a 1,2,3-trisubstituted phenyl group (δ6.71), and intense multiplets of methylene protons of the remaining portion of the molecule (δ1.27, 1.30).

Phenol derivatives **38** and **39** showed simple mass spectra with a distinct $[M]^+$, *m/z* 107, 108 and 91 ions. The *m/z* 107 and 108 ions were derived by cleavage of the bond β to the aromatic ring and the MacLafferty rearrangement of the $[M]^+$. This means that these compounds are monohydric phenols substituted by a long alkyl side chain. They also include a monoalkylphenyl group since a tropylium ion (*m/z* 91) was detected in the mass spectrum. In their IR spectra, absorption bands due to out-of-plane bending deformation of 1,3-disubstituted benzene (750 and 790 cm^{-1}) and that of monosubstituted benzene (700 cm^{-1}) were observed. Therefore these compounds are 3-substituted phenols with an ω-phenylalkyl side chain. From its $[M]^+$, phenol **37** was shown to have a C_{10} methylene chain, and phenol **38** a C_{12} methylene chain. Phenol **40** showed an IR band due to a keto function at 1700 cm^{-1}, and a mass spectral fragment of *m/z* 245 attributable to α-cleavage with loss of a hydroxybenzyl group. In the ^1H NMR spectrum were observed a singlet of methylene protons at the 1′ position (δ3.51) and two triplets due to methylene protons at the 3′ (δ2.42) and 12′ positions (δ2.60). From these data, the unique structure of phenol **40** has been elucidated.

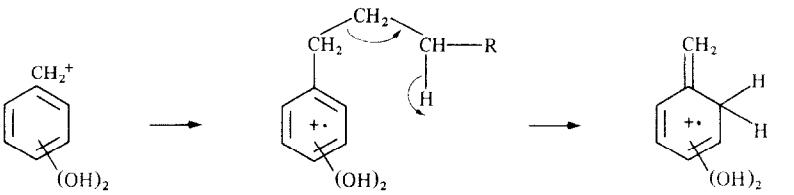
Phenols **35**–**37**, **41** and **42** were obtained in very small amounts in mixtures, and were characterized solely by GC-MS measurement. The *m/z* 107 and 108 ions were common to their mass spectra, implying that these compounds are monohydric alkylphenols. A cardanol homologue (**35**) showed a series of fragment ions characteristic of *n*-alkenes and was revealed to be substituted with a heptadecadienyl group from its $[M]^+$ at *m/z* 328. Compounds **36** and **37** showed relatively weak $[M]^+$ ions (*m/z* 370 and 372) and *m/z* 263 and 265 ions, all of which were accompanied by fragment ions formed by elimination of water. It was then elucidated that they have a hydroxyl group at C-2′ in the side chain. The number of carbon atoms and double bonds in the side chain was determined from the corresponding $[M]^+$ value.

Compound **41** exhibited in its mass spectrum an $[M]^+$ at *m/z* 380 and a fragment ion at *m/z* 273, suggesting that it contains a keto function at the 2′ position. In the mass spectrum of compound **42** an $[M]^+$ at *m/z* 382 and a fragment ion at *m/z* 275, together with ions derived by loss of water, were observed, indicating that it has a hydroxy group at the 2′ position. The substitution position of these minor constituents was tentatively assigned to *meta* considering the biosynthetic route proposed for the formation of phenolic lipids [12, 13].

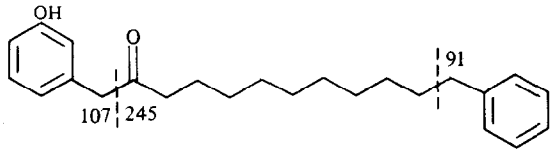
The content of each constituent is listed in Table 1. The main constituents of the sap of *M. usitate* are dienoic thitsiol (**17**), dienoic laccol (**23**), 3-(10′-phenyldecyl)catechol (**31**) and 3-(12′-phenyldodecyl)catechol (**32**).

It is interesting to note that compounds **17** and **23** contain the same side chain, an 8′*Z*,11′*Z*-heptadecyl group, and that of olefinic structure of this substituent is identical with that of linoleic acid. This fact may imply that the ubiquitously distributed fatty acid is a precursor of phenolic lipids in the biosynthetic polyketide pathway [12, 13]; monohydric phenol **35** may possibly be an intermediate of the biosynthesis.

The final step in this route may proceed by enzymatically controlled hydroxylation. In sap of the Burmese lac tree two different enzyme assemblies may exist which give rise to hydroxylation at the 2 and 6 positions of the intermediate **35**. However, this is not peculiar to *M. usitate*; in sap of the Japanese lac tree (*Rhus vernicifera*), 4-(pentadecatrienyl)-catechols with the same side



m/z 123 *m/z* 124



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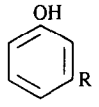


35 R = $C_{17}H_{31}$
36 R = $CH_2CH(OH)C_{17}H_{29}$
37 R = $CH_2CH(OH)C_{17}H_{31}$
38 R = $(CH_2)_{10}Ph$
39 R = $(CH_2)_{12}Ph$
40 R = $CH_2CO(CH_2)_{10}Ph$
41 R = $CH_2CO(CH_2)_{12}Ph$
42 R = $CH_2CH(OH)(CH_2)_{12}Ph$

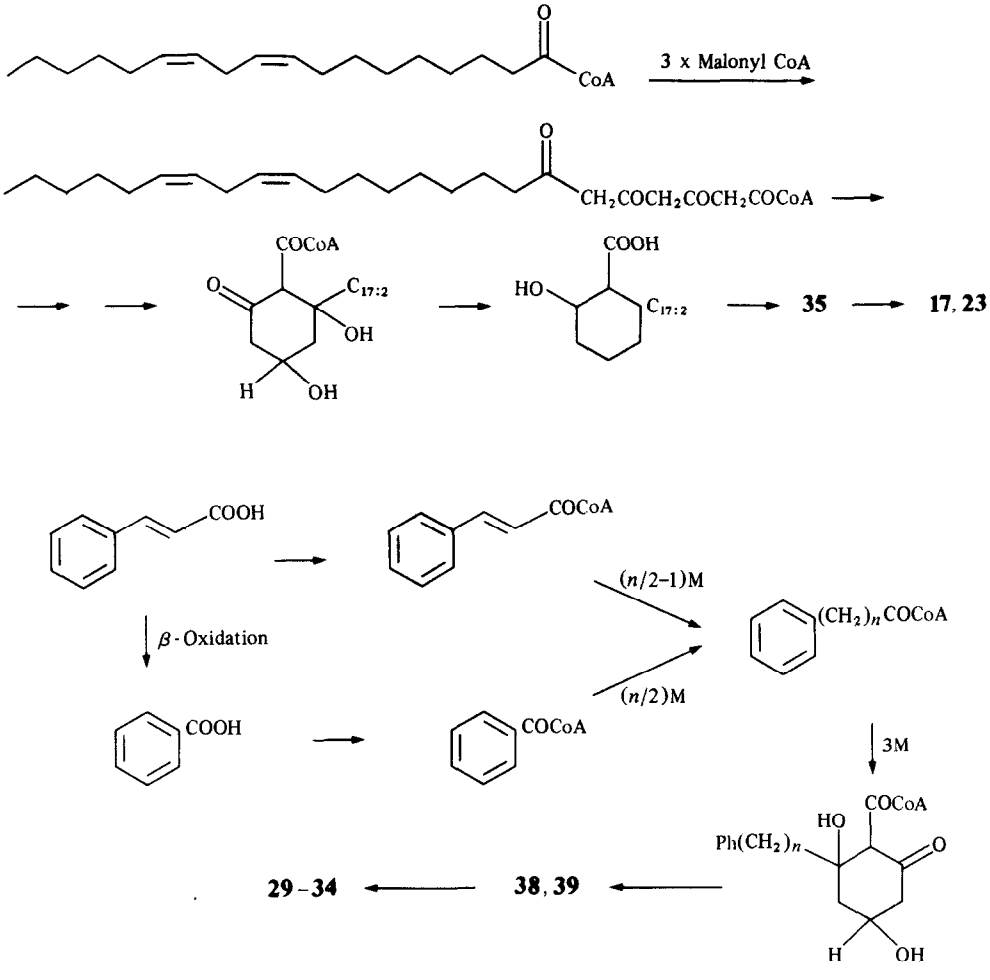
chain olefinic structure as those of urushiol are found although in extremely small amounts [5].

Compounds **29–34** are novel phenolic lipids having an ω-phenyl group in the side chain. Cinnamic acid and benzoic acid derived therefrom by β-oxidation are possible precursors of these characteristic long chain phenols as in the case of biosynthesis of flavonoids [14].

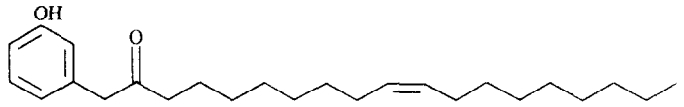
Monohydric phenols **38** and **39** may be regarded as a plausible intermediates in the above biosynthetic pathway. Apart from hydroxylation of the intermediate **35**, that on phenol **38** or **39** occurs preferentially at the 2 position producing the main constituents **31** and **32**, and hydroxylation at the 5 position also proceeds leading to the formation of resorcinols **33** and **34**. Cinnamic and benzoic acids are derived by the shikimic acid pathway through prephenic acid and phenylalanine [15]. Accordingly, ω-phenylalkylcatechols **29–32** and ω-phenylalkylresorcinols **33** and **34** are derived by two consecutive biosynthetic routes, the shikimic acid and polyketide routes.

Compounds **40** and **41** are curious phenolic lipids having a keto function at the position β to the phenol ring. Campnospermanol (**43**), found in *Campnospermum auriculate*, is also known to have a keto function [16].

These unusual phenolic lipids along with minor con-



M = Malonyl CoA



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stituents **36**, **37** and **42**, which contain a hydroxyl group at the 2′ position, are by-products of the biosynthesis of phenolic lipids of sap of *M. usitate*. The keto and hydroxyl functions at the 2′ position are a direct consequence of cyclization of the polyketide precursor [17].

EXPERIMENTAL

Spectroscopy. ^{1}H NMR spectra were measured at 400 MHz and 90 MHz, ^{13}C NMR spectra at 25 MHz.

Chromatography. A self-constructed LC was employed, details of which are described in refs [4, 5]. GC was carried out on an FID instrument equipped with OV-1 fused-silica capillary column (0.2 mm i.d. × 12.5 m) using conditions described in ref. [18].

Separation. Two kinds of natural sap were collected from trees of *M. usitate* grown at Pagan or Nyaung-do (Mandalay State) and Hsuphang (Shan State) in Burma by the traditional method [17] in 1982. They were obtained by the courtesy of the Southsea Association (Tokyo). Two different samples were revealed to comprise same constituents, and we described here the result obtained for the sap from Mandalay state.

Sap was mixed with a three-fold amount of Me_2CO and the mixture stirred for 1 hr followed by filtration through a filter paper. The filtrate was evapd below 40°, dissolved in $CHCl_3$ and the soln subjected to gel permeation chromatography (column, TSK-gel G2000H$_6$, 2.2 × 60 cm; eluant, $CHCl_3$; detection, RI) to obtain a monomeric fraction (yield 45 wt%). Methylation was carried out with Me_2SO_4 in dry Me_2CO at 60° for 5 hr in the presence of K_2CO_3. Hydrogenation was conducted using hydrazine-hydrate in MeOH at 40° for 1 hr. The methylated and hydrogenated sample and the methylated one were resolved on an ODS-silica gel column (Unisil Q C-18, 5 μm, 0.8 × 25 cm) using MeCN–H_2O as eluant and further on a silica gel column (Develosil 60-5, 5 μm, 0.8 × 25 cm) using *n*-hexane–EtOAc (24:1) as eluant. The intact sample was sepd on an ODS-silica gel column (TSK-gel LS-410, 5 μm, 0.8 × 25 cm) using MeCN–H_2O–HOAc as eluant. The purity of separate fractions was examined by capillary GC; minor fractions with several components were analysed by GC-MS.

The location of olefinic bonds in the side chains of compounds **11**–**14** was determined by reductive ozonolysis. The compounds were partly reduced by hydrazine-hydrate in MeOH at 40°. The monoenoic component formed during the partial reduction was collected by reversed-phase HPLC and subjected to micro-ozonolysis in CH_2Cl_2 followed by subsequent reduction with triphenylphosphine and treatment with 2,4-dinitrophenyl-hydrazine [4]. The sample obtained was analysed by reversed-phase chromatography and comparison with R_ts of 2,4-dinitrophenyl hydrazones of standard *n*-alkanals.

4-*Heptadecatrienylcatechol* (**15**). IR ν_{max}^{film} cm^{-1}: 3400, 850, 810; MS (70 eV) *m/z* (rel. int.): 342 [M]$^+$ (14%), 163 (16), 135 (16), 124 (36), 123 (100), 67 (34), 41 (32).

4-trans-*Heptadecatrienylcatechol* (**16**). IR ν_{max}^{film} cm^{-1}: 3400, 960, 860, 810; MS (70 eV) *m/z* (rel. int.) 342 [M]$^+$ (13%), 163 (7), 136 (15), 135 (10), 124 (11), 123 (100), 107 (7), 95 (28), 79 (25), 67 (18), 55 (15), 41 (20).

4-[8′Z,11′Z-*Heptadecadienyl*]*catechol* (**17**). IR ν_{max}^{film} cm^{-1}: 3400, 860, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ6.64 (*d*, 1H, *J* = 8.4 Hz, H-6), 6.62 (*d*, 1H, *J* = 2.7 Hz, H-3), 6.54 (*dd*, 1H, H-5), 5.36 (*m*, 4H, H-8′, 9′, 11′, 12′), 2.78 (*m*, 2H, H-10′), 2.49 (*t*, 2H, *J* = 8 Hz, H-1′), 2.03 (*m*, 4H, H-7′, 13′), 1.59 (*m*, 2H, H-2′), 1.31 (*m*, 14H, H-3′–6′, 14′–16′), 0.89 (*t*, 3H, H-17′); MS (70 eV) *m/z* (rel. int.): 344 [M]$^+$ (10%), 136 (24), 124 (24), 123 (100), 95 (22), 81 (24), 67 (46), 55 (34), 41 (49).

O-*Dimethyl*-4-[8′Z,11′Z-*heptadecadienyl*]*catechol* (**11**). Mp 56–57°; IR ν_{max}^{film} cm^{-1}: 850, 810; MS (70 eV) *m/z*: 372 [M]$^+$.

4-trans-*Heptadecatrienylcatechol* (**18**). IR ν_{max}^{film} cm^{-1}: 3400, 960, 860, 810; MS (70 eV) *m/z* (rel. int.): 346 [M]$^+$ (25%), 124 (31), 123 (100).

4-cis-*Pentadecenylcatechol* (**19**). IR ν_{max}^{film} cm^{-1}: 3400, 860, 810; MS (70 eV) *m/z* (rel. int.): 318 [M]$^+$ (35%), 136 (40), 124 (43), 123 (100), 69 (11), 55 (24), 41 (29).

4-*Pentadecylcatechol* (**20**). Mp 67° (lit. 67–68° [10]); IR ν_{max}^{film} cm^{-1}: 3400, 860, 810; MS (70 eV) *m/z* (rel. int.): 320 [M]$^+$ (50%), 136 (10), 124 (55), 123 (100).

O-*Dimethyl*-4-*heptadecylcatechol* (**2**). Mp 56–57° (lit. 56–57° [10]); IR ν_{max}^{film} cm^{-1}: 650, 810; MS (70 eV) *m/z*: 376 [M]$^+$.

O-*Dimethyl*-4-*pentadecylcatechol* (**1**). Mp. 42–43°; IR ν_{max}^{film} cm^{-1}: 850, 810; MS (70 eV) *m/z* (rel. int.): 348 [M]$^+$ (97%), 152 (55), 151 (100), 137 (9), 95 (7), 81 (19), 71 (10), 69 (38), 67 (8), 57 (11), 55 (14), 43 (20), 41 (14).

3-*Heptadecatrienylcatechol* (**21**). IR ν_{max}^{film} cm^{-1}: 3400, 770, 730; MS (70 eV) *m/z* (rel. int.): 342 [M]$^+$ (3%), 163 (8), 124 (13), 123 (100), 95 (25), 79 (32), 67 (25), 55 (22), 41 (22).

3-trans-*Heptadecatrienylcatechol* (**22**). IR ν_{max}^{film} cm^{-1}: 3400, 970, 770, 730; MS (70 eV) *m/z* (rel. int.): 342 [M]$^+$ (7%), 163 (9), 124 (15), 123 (100), 95 (27), 81 (18), 79 (38), 77 (10), 67 (29), 55 (13), 41 (22).

3-[8′Z,11′Z-*Heptadecadienyl*]*catechol* (**23**). IR ν_{max}^{film} cm^{-1}: 3400, 770, 730; MS (70 eV) *m/z* (rel. int.): 344 [M]$^+$ (5%), 136 (27), 124 (26), 123 (100), 95 (20), 81 (22), 67 (38), 55 (27), 41 (35).

O-*Dimethyl*-3-[8′Z,11′Z-*heptadecadienyl*]*catechol* (**12**). Mp 42–43°; IR ν_{max}^{film} cm^{-1}: 3400, 745; MS (70 eV) *m/z*: 372 [M]$^+$.

3-[8′(Z)- *and* 10′(Z)-*Heptadecenyl*]*catechol* (**24**). IR ν_{max}^{film} cm^{-1}: 3400, 770, 730; MS (70 eV) *m/z* (rel. int.): 346 [M]$^+$ (14%), 136 (30), 124 (33), 123 (100).

O-*Dimethyl*-3-[8′Z- *and* 10′Z-*heptadecenyl*]*catechol* (**13**) *and* **14**. IR ν_{max}^{film} cm^{-1}: 745; MS (70 eV) *m/z* 374 [M]$^+$.

3-trans-*Heptadecenylcatechol* (**25**). IR ν_{max}^{film} cm^{-1}: 3400, 960, 770, 730; MS (70 eV) *m/z* (rel. int.): 346 [M]$^+$ (16%), 136 (32), 124 (94), 123 (100).

3-*Pentadecadienylcatechol* (**26**). IR ν_{max}^{film} cm^{-1}: 3400, 770, 730; MS (70 eV) *m/z* (rel. int.): 316 [M]$^+$ (43%), 136 (34), 124 (30), 123 (100), 83 (35), 71 (70), 56 (95), 54 (80).

3-*Pentadecenylcatechol* (**27**). IR ν_{max}^{film} cm^{-1}: 3400, 770, 730; MS (70 eV) *m/z* (rel. int.): 318 [M]$^+$ (33%), 136 (39), 124 (41), 123 (100), 55 (24), 41 (28).

3-*Pentadecylcatechol* (**28**). Mp 58° (lit 58–59° [10]); IR ν_{max}^{film} cm^{-1}: 770, 730; MS (70 eV) *m/z* (rel. int.): 320 [M]$^+$ (57%), 124 (52), 123 (100), 85 (9), 71 (16), 56 (25).

O-*Dimethyl*-3-*heptadecylcatechol* (**3**). Mp 42–43° (lit. 43–44° [10]); IR ν_{max}^{film} cm^{-1}: 750; MS (70 eV) *m/z*: 376 [M]$^+$.

O-*Dimethyl*-3-*pentadecylcatechol* (**4**). Mp 35–36° (lit. 36–37°

[10]); IR ν_{max}^{film} cm^{-1}: 750; MS (70 eV) *m/z*: 348 $[M]^+$.

4-(10′-*Phenyldecyl*)*catechol* (**29**). IR ν_{max}^{film} cm^{-1}: 3400, 850, 700; MS (70 eV) *m/z* (rel. int.): 326 $[M]^+$ (43%), 136 (5), 124 (31), 123 (100), 91 (25), 77 (8), 65 (5), 55 (4), 41 (8).

O-*Dimethyl*-4-(10′-*phenyldecyl*)*catechol* (**5**). Mp 47.5–48°; IR ν_{max}^{KBr} cm^{-1}: 850, 810, 700; ^1H NMR (90 MHz, CCl_4) δ7.13 (*br s*, 5H, phenyl-H), 6.66 (*m*, 3H, H-3, 5,6), 3.72 (*s*, 3H, OMe), 3.70 (*s*, 3H, OMe), 2.56 (*t*, 2H, *J* = 8 Hz, H-10′), 2.48 (*t*, 2H, *J* = 8 Hz, H-1′), 1.6 (*m*, 4H, H-2′, 9′), 1.27 (*br s*, 12H, H-3′-8′).

4-(12′-*Phenyldodecyl*)*catechol* (**30**). IR ν_{max}^{film} cm^{-1}: 3400, 850, 810, 700; MS (70 eV) *m/z* (rel. int.): 354 $[M]^+$ (50%), 124 (40), 123 (100), 91 (30).

O-*Dimethyl*-4-(12′-*phenyldodecyl*)*catechol* (**6**). Mp 56–57°; IR ν_{max}^{KBr} cm^{-1}: 850, 810, 700; ^1H NMR (90 MHz, CCl_4) δ7.13 (*br s*, 5H, phenyl-H), 6.66 (*m*, 3H, H-3, 5,6), 3.72 (*s*, 3H, OMe), 3.70 (*s*, 3H, OMe), 2.56 (*t*, 2H, *J* = 8 Hz, H-12′), 2.48 (*t*, 2H, *J* = 8 Hz, H-1′), 1.6 (*m*, 4H, H-2′,11′), 1.27 (*br s*, 16H, H-3′,10′); MS (70 eV) *m/z* (rel. int.): 382 $[M]^+$ (23%), 194 (5), 165 (24), 152 (100), 151 (27).

3-(10′-*Phenyldecyl*)*catechol* (**31**). (Found: C, 80.89; H, 9.33. Calc. for $C_{22}H_{30}O_2$: C, 80.92; H, 9.26%. Found: $[M]^+$ 326.2230. Calc. 326.2247); IR ν_{max}^{film} cm^{-1}: 3400, 770, 730, 700; ^1H NMR (400 MHZ, $CDCl_3$): δ7.18 (*m*, 3H, H-2″, 4″, 6″), 7.17 (*m*, 2H, H-3″, 5″), 6.71 (*br s*, 3H, H-4,5,6), 5.08 (*s*, 1H, OH), 4.95 (*s*, 1H, OH), 2.59 (*t*, 4H, H-1′, 10′), 1.60 (*m*, 4H, H-2′, 9′), 1.30 (*m*, 4H, H-3′, 8′), 1.27 (*m*, 8H, H-4′-7′); ^{13}C NMR (25 MHz, $CDCl_3$): δ142.9 (C-1, 1″), 141.8 (C-2), 129.4 (C-3), 128.4 (C-3″, 5″), 128.2 (C-2″, 6″), 125.5 (C-4″), 122.1 (C-5), 120.1 (C-4), 112.9 (C-5), 36.0 (C-10′), 31.5 (C-1′), 29.5 (C-2′ -9′); MS (70 eV) *m/z* (rel. int.): 326 $[M]^+$ (95%), 124 (100), 123 (95), 91 (58).

3-(10′-*Phenyldecyl*)*veratrole* (**7**). IR ν_{max}^{film} cm^{-1}: 750, 700; ^1H NMR (90 MHz, CCl_4): δ7.13 (*br s*, 5H, phenyl-H), 6.9–6.6 (*m*, 3H, H-4,5,6), 3.82 (*s*, 3H, MeO), 3.77 (*s*, 3H, MeO), 2.58 (*m*, 4H, H-1′, 10′), 1.6 (*m*, 4H, H-2′, 9′), 1.27 (*br s*, 12H, H-3′–8′); MS (70 eV) *m/z*: 354 $[M]^+$.

3-(12′-*Phenyldodecyl*)*catechol* (**32**). Mp 65° (Found: C, 81.21; H, 9.60. Calc. for $C_{24}H_{34}O_2$: C, 81.30; H, 9.67. Found: $[M]^+$ 354.2560. Calc. 354.2560); IR ν_{max}^{film} cm^{-1}: 3400, 770, 730, 700; ^1H NMR (400 MHz, $CDCl_3$): δ7.18 (*s*, 3H, H-2″, 4″, 6″), 7.17 (*m*, 2H, H-3″, 5″), 6.71 (*s*, 3H, H-4,5,6), 5.08 (*s*, 1H, OH), 4.95 (*s*, 1H, OH), 2.59 (*t*, 4H, *J* = 8 Hz, H-1′, 12′), 1.60 (*m*, 4H, H-2′, 11′), 1.30 (*m*, 4H, H-3′, 10′). 1.27 (*m*, 12H, H-4′ -9′); ^{13}C NMR (25 MHz, $CDCl_3$): δ142.9 (C-1, C-1″), 141.8 (C-2), 129.4 (C-3), 128.3 (C-3″, 5″), 128.2 (C-2″, 6″), 125.5 (C-4″), 122.1 (C-5), 120.1 (C-4), 112.9 (C-5), 36.0 (C-12′), 31.5 (C-1′), 29.5 (C-2′-11′); MS (70 eV) *m/z* (rel. int.): 354 $[M]^+$ (100%), 124 (91), 123 (92), 91 (51).

3-(12′-*Phenyldodecyl*)*veratrole* (**8**). IR ν_{max}^{film} cm^{-1}: 750, 700; ^1H NMR (90 MHz, CCl_4): δ7.13 (*br s*, 5H, phenyl-H), 6.9–6.6 (*m*, 3H, H-4,5,6), 3.82 (*s*, 3H, MeO), 3.77 (*s*, 3H, MeO), 2.58 (*br t*, 4H, H-1′ and 12′), 1.6 (*m*, 4H, H-2′ and 11′), 1.27 (*br s*, 16H, H-3′–10′; MS (70 eV) *m/z* (rel. int.): 382 $[M]^+$ (100%), 152 (97), 151 (90), 137 (50), 136 (73), 121 (20), 105 (8), 91 (90), 77 (9), 55 (8), 41 (15).

5-(10′-*Phenyldecyl*)*catechol* (**33**). (Found: $[M]^+$ 326.2264. Calc. for $C_{22}H_{30}O_2$: 326.2247); IR ν_{max}^{film} cm^{-1}: 830, 700; MS (70 eV) *m/z* (rel. int.): 326 $[M]^+$ (22%), 124 (100), 123 (22), 91 (40).

O-*Dimethyl*-5-(12′-*phenyldecyl*)*resorcinol* (**9**). Mp 30–31°; IR ν_{max} cm^{-1}: 830, 700; ^1H NMR (90 MHz, CCl_4): δ7.10 (*br s*, 5H, phenyl-H), 6.15 (*br s*, 3H, H-2,4,6), 3.68 (*s*, 6H, OMe), 2.56 (*t*, 2H, *J* = 8 Hz, H-10′), 2.47 (*t*, 2H, *J* = 8 Hz, H-1′), 1.6 (*m*, 4H, H-2′,9′), 1.27 (*br s*, 12H, H-3′–8′); MS (70 eV) *m/z* (rel. int.): 382 $[M]^+$ (73%), 151 (100), 137 (8), 121 (5), 107 (6), 91 (32), 79 (5), 67 (8), 55 (8), 41 (8).

5-(12′-*Phenyldodecyl*)*resorcinol* (**34**). IR ν_{max}^{film} cm^{-1}: 830, 700; MS (70 eV) *m/z* (rel. int.): 354 $[M]^+$ (25%), 124 (100), 123 (35), 91 (30).

O-*Dimethyl*-5-(12′-*phenyldodecyl*)*resorcinol* (**10**). IR ν_{max}^{film} cm^{-1}: 830, 700; ^1H NMR (90 MHz, CCl_4): δ7.10 (*br s*, 5H, phenyl-H), 6.15 (*br s*, 3H, H-2, 4, 6), 3.68 (*s*, 6H, OMe), 2.56 (*t*, 2H, *J* = 8 Hz, H-12′), 2.47 (*t*, 2H, *J* = 8 Hz, H-1′), 1.6 (*m*, 4H, H-2′,11′), 1.27 (*br s*, 16H, H-3′-10′); MS (70 eV) *m/z* (rel. int.): 382 $[M]^+$ (73%), 165 (5), 152 (24), 151 (100), 137 (11), 121 (5), 107 (6), 91 (32), 81 (5), 67 (8), 55 (8), 43 (8), 41 (8).

3-*Heptadecadienylphenol* (**35**). MS (70 eV) *m/z* (rel. int.): 328 $[M]^+$ (13%), 147 (27), 133 (17), 120 (48), 108 (100), 107 (93), 95 (25), 81 (40), 79 (34), 77 (35), 67 (74), 55 (52), 41 (80).

3-(2′-*Hydroxynonadecatrienyl*)*phenol* (**36**). MS (70 eV) *m/z* (rel. int.): 370 $[M]^+$ (5%), 352 $[M - H_2O]^+$ (15), 263 (27), 245 (12), 135 (10), 123 (14), 109 (23), 108 (18), 107 (58), 95 (47), 81 (66), 67 (100), 55 (86), 41 (77).

3-(2′-*Hydroxynonadecadienyl*)*phenol* (**37**). MS (70 eV) *m/z* (rel. int.): 372 $[M]^+$ (3%), 354 $[M - H_2O]^+$ (6%), 265 (5), 108 (100), 107 (19), 81 (15), 67 (23), 55 (25), 41 (24).

3-(10′-*Phenyldecyl*)*phenol* (**38**). IR ν_{max}^{film} cm^{-1}: 3400, 790, 750, 700; MS (70 eV) *m/z* (rel. int.): 310 $[M]^+$ (14%), 108 (100), 107 (35), 91 (56).

3-(12′-*Phenyldodecyl*)*phenol* (**39**). (Found: $[M]^+$ 338.2600. Calc. for $C_{24}H_{34}O$: 338.2611); IR ν_{max}^{film} cm^{-1}: 3400, 790, 750, 700; MS (70 eV) *m/z* (rel. int.): 338 $[M]^+$ (30%), 121 (10), 108 (100), 107 (42), 91 (24).

3-(2′-*Oxo*-12′-*phenyldodecyl*)*phenol* (**40**). (Found: $[M]^+$ 352.2391. Calc. for $C_{24}H_{32}O_2$: 352.2404); IR ν_{max}^{film} cm^{-1}: 3400, 1700, 790, 750, 700; ^1H NMR (400 MHz, $CDCl_3$): δ7.18 (*br s*, 3H, H-2″, 4″, 6″), 7.17 (*br s*, 2H, H-3″, 5″), 6.75 (*m*, 4H, H-2, 4, 5, 6), 4.88 (*s*, 1H, OH), 3.51 (*s*, 2H, H-1′), 2.60 (*t*, 2H, *J* = 8 Hz, H-12′), 2.42 (*t*, 2H, *J* = 8 Hz, H-3′), 1.30 (*br s*, 4H, H-4′, 11′), 1.27 (*br s*, 12H, H-5′-10′); MS (70 eV) *m/z* (rel. int.): 352 $[M]^+$ (7%), 245 (25), 131 (20), 117 (9), 108 (27), 107 (13), 91 (100), 41 (10).

3-(2′-*Oxo*-14′-*phenyltetradecyl*)*phenol* (**41**). MS (70 eV) *m/z* (rel. int.): 380 $[M]^+$ (20%), 273 (32), 159 (5), 131 (16), 117 (2), 107 (18), 91 (100).

3-(2′-*Hydroxy*-14′-*phenyltetradecyl*)*phenol* (**42**). MS (70 eV) *m/z* (rel. int.): 382 $[M]^+$ (1%), 364 $[M - H_2O]^+$ (2), 275 (3), 257 $[275 - H_2O]^+$ (0.8), 131 (8), 108 (100), 91 (28).

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